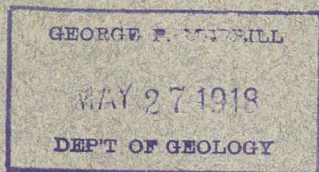


Merwin, H. E.

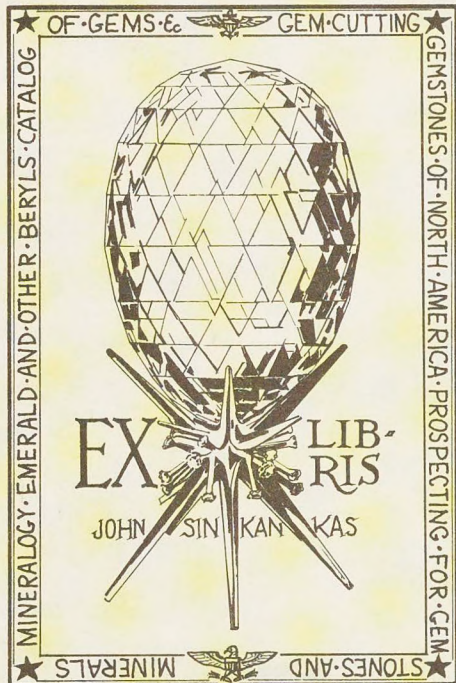
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Optical Properties and Theory of Color of Pigments and Paints.

By H. E. MERWIN.

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OPTICAL PROPERTIES AND THEORY OF COLOR OF PIGMENTS AND PAINTS.

BY H. E. MERWIN.

SUMMARY.

The hue, purity and brightness of light diffused by a pigment or paint depends upon the refractive index, color absorption, size, shape and texture of the pigment grains, and upon the refractive index, color, and continuity of the vehicle; and also upon the distribution of the grains in the vehicle.

A black pigment to be most effective optically should have (1) a refractive index equal to that of the surrounding medium, and (2) grains $1\ \mu$ (or less) in diameter¹ which should be (3) just barely opaque to all colors. All the ordinary black pigments possess the third characteristic approximately, some of them the second, but only one of them, bone black in its various forms, has approximately the best refractive index.

A white pigment should have a high refractive index, should be even grained, with grains about 0.5 to $1.0\ \mu$ in diameter. Finer grains diffuse blue light more than red light under certain conditions, for example, when mixed in oil with black or dark red pigments. Thus blue grays and purples result. Most white pigments contain enough very fine grains to give bluish grays. Control of size of grain is important. It is probable that the refractive index of certain zinc oxides made by the American process can be controlled advantageously.

Coloring efficiency must be considered as much from the standpoint of the hue and tone desired as of the absolute "quantity of color" obtained. Thus, although extremely fine division may favor the last factor mentioned, when the pigment

¹ The term μ is the symbol for a micron ($0.001 = \text{mm.}$).

is used in a mixture with a strongly diffusing pigment, yet under other conditions size and shape of grain and refractive index are of great importance. For example, Harrison red in grains of one shape has about 10 per cent better diffusing power than in grains of another shape. The shifting of hue, especially of orange and yellow paints toward the green, due to admixed black is considered in detail. The optical properties which determine whether a pigment is best suited for producing tints or shades are discussed.

Special methods of studying the optical properties of pigments have been used, and a considerable number of optical constants determined. These properties can be applied in determinative work or to problems in chromatics.

This investigation has been conducted in the Geophysical Laboratory of the Carnegie Institution of Washington.

OPTICAL PROPERTIES AND THEORY OF COLOR OF PIGMENTS AND PAINTS.¹

BY H. E. MERWIN.

I. INTRODUCTION.

Color is commonly described in terms of hue, purity and brightness, which respectively characterize color with regard to the position of its equivalent or complementary in the spectrum; the amount of admixed white light; its brilliancy compared with a standard white. Another term to designate a pure hue of maximum brightness is desirable. The term "full color," which has been used in an indefinite way, will be used here in this definite sense.² The brightness of a paint may be decreased by admixture of a black pigment. For present purposes the color of a pigment or paint is known adequately if the percentages of full color, white, and black are given.

Ridgway's³ color standards are constructed on a theoretical basis similar to that just outlined. The standards themselves are not of theoretical purity or fullness, but they are excellent for comparative tests, and have proved satisfactory in the experimental work later described. All the direct comparisons of color herein are based upon them.

II. GENERAL OPTICAL RELATIONSHIPS OF PIGMENTS.

Under standard conditions of observation the optical properties of a painted surface depend upon the pigment, the vehicle and the surface covered. Here, surfaces will be considered only incidentally; vehicles will be considered in relation

¹ This study was suggested by P. H. Walker, chairman of Committee D-1 of the Society, who furnished the writer with many of the pigments examined.

See a short paper by Wilhelm Ostwald, *Kolloid Zeitschr.*, Vol. 16, pp. 1-4 (1915).

² A pure hue, which is equivalent to a single wave-length, can be produced by combining light of a series of wave-lengths on one side of the equivalent wave-length with another series on the other side. A full color results when a maximum amount of such light is combined. Wave-lengths beyond the range of these two series act as complementary to some of those present, and thus introduce white. The lightness of some yellows—barium yellow, for example—is due in part to the presence of the complementaries blue-green and red.

³ Robert Ridgway, "Color Standards and Color Nomenclature," Washington, D. C., 1912.

to the optical phenomena of pigments. Attention will be directed chiefly to pigments.

A property common to all pigments and painted surfaces, that of diffusing light, must be considered in almost every problem concerning the optical properties of paints and pigments. This property is a complex result of certain fundamental relations of properties of pigment grains and surrounding vehicle, or other medium. Grains must be considered with respect to refractive index, color absorption,¹ size, shape, and texture; dried vehicles with respect to refractive index, color absorption and quality of surface. The amount of light reflected from a unit area of surface of a grain or of a paint vehicle increases with the refractive index and absorbing power. The effective reflecting surface of a given volume of pigment increases with the fineness of grain until the grains become too small to act as regular reflectors, that is, when their diameter is about the length of a wave of light in the medium containing the pigment. Smaller grains scatter light, but scattering is not as efficient as reflection. (See Section X.)

III. OPTICAL RELATIONS OF VEHICLE TO PIGMENT.

Dried oil, varnish and albumen have refractive indices of about 1.5, and smooth surfaces reflect about 4 per cent of the light which falls perpendicularly upon them. Minutely rough, "flat" surfaces produced by drying would reflect about the same amount, even if the effects of the enclosed pigment and underlying surface were eliminated. Thus, the "blackness" of a black paint is limited by the reflecting power of the vehicle. Pigment grains surrounded by a vehicle reflect less than in air,² because the ratio of refractive index of grain to surrounding medium is less. The most general consequence of this is to cause light which enters the surface of a film of paint to traverse more pigment grains before it returns through the surface, than it would traverse if the pigment grains were surrounded by air.

¹ The purpose of the following sections is to indicate essentially the significance of certain other factors than color absorption which enter into the problems of color of paints. Rood ("Modern Chromatics") devised several experiments to show effects of some of these factors, but some of his interpretations need revision. Color is discussed from many view-points, and lists of reference are included in "Color and its Applications," by M. Luckiesh, 1915.

² There are possible exceptions in the case of pigments with metallic reflection.

Thus, more light may be absorbed and the paint appear darker than the dry pigment. (See Sections IV and XV.) The wavelength of a given color of light is less in paint vehicles than in air. Thus, grains of a given size scatter light differently in these different media. (See Section X.) The use of colored vehicles and glazing colors is discussed later.

IV. REFLECTION, AND PRIMARY AND SECONDARY DIFFUSION OF LIGHT BY PIGMENTS.

Light striking a pigment grain is partly reflected or scattered without traversing the grain, is partly absorbed and partly transmitted to the far side of the grain where some emerges and some is reflected within the grain. Several grains in succession may take part in turning back into the air what is left of light which had penetrated a mass of paint or pigment. Light which has been returned into the air without traversing any pigment grains will be called primarily diffused light; light which has traversed grains before being returned will be called secondarily diffused light. From pigments with metallic luster—opaque pigments such as aluminum, gilt, bronze and graphite—light is primarily diffused; from ordinary transparent pigments light is diffused in both ways, but in greater part secondarily.

V. COLOR ABSORPTION AND SIZE OF GRAIN.

An adequate discussion of the colors of pigments must be based upon knowledge of the color absorption of single pigment grains. Most pigments, except lakes, consist of minute crystals. Variation of color with direction in crystals is common (pleochroism). Therefore, the shape of crystals may determine their value as constituents of a pigment. For example, one factor in the variation in color of red leads is the shape of the crystals with respect to their color axes. Also, "permanent" violet would have much more coloring power if its crystals were flattened in a different direction.

The boundary in the spectrum between wave-lengths (spectral hues) that are strongly absorbed, and those that are freely transmitted by a pigment substance, is always so wide that small grains transmit considerable light that would be absorbed

by large grains.¹ A pigment consisting of small grains tends to be brighter and have a hue represented by a wave-length nearer an absorption band, than a pigment consisting of large grains.² (Fig. 7.)

Two extreme types of light transmission deserve consideration. In one, large grains are highly transparent to hues which characterize their color; in the other, even the characteristic hues are largely absorbed by small grains. Examples of the first are chrome yellows, red lead, cobalt blue and emerald green; of the second, ferric oxide and chromic oxide.

Coloring power increases as size of grain decreases, but at very different rates for different substances.³ The rate for a given substance depends upon the method of diffusing the color and upon the extent of dilution of the color. Diffusion may be brought about by the surface over which the paint is spread (glazing colors), or by admixed grains having diffusing power, or by the pigment grains themselves. Maximum coloring power cannot be expected if single grains—or two superposed grains in case of intermediate hues of mixtures—are more deeply colored than the final diffused color sought. On the other hand there is little advantage in having grains much finer than this unless the diffusing power improves with fineness. From this it would appear that two samples of the same pigment may have different coloring power when mixed with a large excess of white or when used as glazing color, and yet not be appreciably different when used in making nearly full colors or shades.

If the grain size of a secondarily diffusing colored pigment could be gradually decreased below the optimum, the resulting paint would become first a turbid medium and then it would clear until it appeared like a colored solution. There is no good

¹ In cases where the terms large, small, etc., have needed more definite limitation about the following limits have been in mind: very small, less than 0.8 μ ; small, 0.8 to 2 μ ; medium, 2 to 5 μ ; large, 5 to 10 μ ; very large, greater than 10 μ .

² Most colored pigments do not contain significant amounts of separate grains smaller than 0.5 μ or larger than 10 μ in mean diameter. Prussian blue is often exceptionally fine grained, and emerald green, verdigris, true cobalt blue, some lakes and some natural pigments are exceptionally coarse grained.

³ For a given amount of pigment the amount of surface exposed to intercept light increases inversely as the square of the diameter of the grains, whereas the power of a grain to modify transmitted light in any direction increases more slowly than the diameter. A crystal of potassium chromate or of copper sulfate 1 mm. in thickness has about as much depth of color as one 5 mm. thick. Pigments of the first type above mentioned are less affected by changes of grain than the second.

evidence that marked changes in hue in a particular direction would take place during the process. In the latter condition it would possess the maximum coloring power if used as a glazing color.

Somewhat at the expense of coloring efficiency the hue of a paint can be slightly controlled by controlling the size of grain. Grains of an even size are better, because larger grains absorb excessively. Basic lead chromate in medium-size grains is scarlet, but in medium to small grains it is nearly orange. (See Section XVII.)

With regard to the adaptability of colored pigments to the making of tints and shades, four classes of pigments may be considered. (See Sections II, XIII and XIV.)

1. Colored grains are chiefly of such size that if closely packed in a single layer they would transmit (or diffuse and transmit) a clear tint (say roughly 40 to 60 per cent white). From 5 to 20 such layers would produce a full color. Either clear tints or pure shades can be made from such a pigment. Examples: chrome orange, chrome yellow, verdigris, ultramarine blue.

2. Grains are so transparent that white light after traversing many layers of grains still contains a good deal (20 per cent or more) of white. Such a pigment can be used in making clear tints, but not pure shades. Examples: barium yellow, basic copper carbonate, strontium yellow.

3. A single layer of grains absorbs several per cent of the characteristic hue, and other hues almost completely. Pure shades and dull tints can be made from such a pigment. Examples: vermilion, scarlet chromate, Harrison red, chrome green.

4. Single grains absorb several per cent of the characteristic hue, and even several layers of grains do not absorb other hues completely. When darkened by a black pigment dull shades result, and when lightened by a white pigment dull tints are formed. Examples: Naples yellow, some Dutch pinks and yellow ochres.

In the last two classes diffusing power determines to some extent, and absorbing power to a greater extent, what range of pure shades can be obtained.

A distinction between tint and shade when both black and white modify a hue can not be made on any generally accepted basis. M. Luckiesh¹ favors the idea—which appears most acceptable—that a shade results from diminishing the brightness of the standard hue by means of either gray or black. On this basis a tint would result from increasing the brightness by means of white, or a gray which is brighter than the standard hue. Ridgway selected a definite gray, and considered that lighter grays produce tints and darker grays shades.

VI. RELATION OF COLOR TO REFRACTIVE INDEX.

To be most effective as a pigment when used alone, a substance should have a high refractive index for the color which it most freely transmits. In general there are large variations of refractive index near and through a region of color absorption. Refractive index is higher on the long-wave side of such a region than on the short-wave side. For this reason red, orange, and yellow pigments usually have much higher refractive indices than blue and violet pigments. The refractive index of lakes is largely determined by the base, and is always comparatively low. Some pigments so nearly match vehicles in refractive index that they diffuse very little light. They become effective only when mixed with a pigment of high refractive index which will diffuse their color, or when painted in thin films over a surface covered with a strongly diffusing paint. For example, Prussian blue, verdigris, and alizarine lakes. (See Sections XII and XVII.)

VII. BIREFRINGENCE AND OPTICAL ORIENTATION.

The refractive index of anisotropic crystals varies with direction—birefringence. If birefringence is strong the shape of the crystal may greatly affect its efficiency as a diffuser of light in a mass of pigment. A very noteworthy example is Harrison red. (See Section XVII.) With the refractive index axes of prismatic grains in the most effective positions the diffusing power is about 10 per cent more than with the axes in the least effective positions.

¹"Color and its Applications," New York, 1915, p. 71.

VIII. HIDING POWER.

The standards of the Society define hiding power as the power of a paint or paint material as used to obscure a surface painted with it.

The foregoing considerations indicate the several factors here concerned. Hiding power thus defined increases with increase of the following properties of the pigment: refractive index, fineness (till optimum size is reached), depth of color, and in certain cases with the roughness and complexity of the pigment grains. The hiding power of a paint increases with increase of hiding power of the pigment, with decreasing refractive index of the vehicle, and with increasing depth of color of the vehicle. Mention should be made of slight but indefinable variations due to irregularities of the surface of the paint film, and to the distribution of the pigment¹ throughout the film. It seems probable that the lack of agreement among observers who have compared the hiding power of white pigments is due in part to differences unprovided for in the grain of the pigments.²

IX. THE BLACK PIGMENTS.

A pigment to be really black should have a refractive index the same as the dried vehicle in which it is used, and should have such absorptive power for all colors as would cause incident light to be about all absorbed by particles 1 to 2 μ in diameter. Such absorption power would not give the pigment as held in its vehicle any significant reflecting power. In the dry state such a pigment would reflect a little light, and therefore be a very dark neutral gray. A compact film of paint made from such a pigment would not be absolutely black, for the surface of the vehicle would reflect about 4 per cent of light. A film in which the pigment is held loosely, such as is produced by using a little binding material with a large amount of volatile vehicle, may give a diffuse reflecting power as low as about 0.5 per cent.

Ivory black is very nearly a perfect black. Its refractive index is only slightly greater than oil or varnish, and its absorptive power is such that all except a small percentage of its grains

¹ The pigment grains nearest to the exposed surface of the film are most effective. Compare the effect produced by the ground side of a glass against a surface, with the effect when the glass is reversed.

² Tests on opacity and hiding power of some white pigments have been made by G. W. Thompson, *Journal of Industrial and Engineering Chemistry*, Vol. 5, p. 120 (1913).

are nearly opaque. The sight color transmitted by a single grain is brownish, so that when these grains are mixed with a coarse-grain white (see Section X) a gray is produced that is perceptibly brownish. When used alone, the brown color transmitted by the first grains traversed is absorbed by succeeding grains so that a most intense black results. A thick film of pure Prussian blue, or even ultramarine, in oil is black. In this case the blue is more freely transmitted than the brown of ivory black, but the refractive index of the pigment is so near that of the oil that the blue light is not diffused outward.

The black residue left after extracting the calcium salts from ivory (or bone) black cannot be definitely characterized, but the shrunken and disintegrated grains still have about the same refractive index and absorptive power as ivory black, but they are less dense.

Graphite is not an ideal black pigment because of its high reflecting power. The color of its reflected light¹ is faintly brownish. Its absorption is so strong that the light transmitted by pigment grains is entirely negligible. Repeated reflections within a film of graphite paint cut down the intensity of the diffused light, so that such a film appears very dark neutral gray.

Lampblack and similar blacks are typically composed of practically opaque ovoidal particles about $1\ \mu$ in diameter adhering loosely in strings or clusters. The reflecting powers of these materials are probably not greatly inferior to those of graphite, for when they are compressed strongly against a polished steel surface they reflect well. Their fine state of division gives them great tinting strength.

The sample of magnetic-oxide black which was examined consisted of spheroidal particles, mostly between 0.8 and $1.5\ \mu$ in diameter. These were appreciably transparent in dark to light browns. The refractive index is probably near that of graphite.

Some of the optical effects produced by one of these blacks may not be produced by another. (See Section XI.)

X. THE WHITE PIGMENTS.²

The most important characteristics contributing to the efficiency of a white pigment are non-absorbing power, high

¹ When compared with a neutral gray in a reflecting microscope.

² For details, see Section XVII. A paper by H. A. Gardner is in most respects in accord with this study: *Journal of Industrial and Engineering Chemistry*, Vol. 8, p. 794 (1916.)

refractive index, weak optical dispersion, fineness and evenness of grain. If optical dispersion is strong, the reflecting power for blue and violet light may be so much greater than for red as to give the pigment a bluish color under certain conditions. There is a critical size of grain for each homogeneous white pigment, depending upon the optical properties of the grains and vehicle and the distribution of the pigment grains. This size is from about 0.5 to 1.0 μ . Larger grains have too little reflecting surface per volume of substance, and grains much smaller do not act as regular reflectors at all unless very close together, but they scatter light. Grains having a diameter close to a wave-length of green light in oil—0.35 μ —may reflect violet more strongly than red. Neither scattering, nor the differential reflection just referred to, have significant effect on the tint of a white pigment, provided the grains are close together and in a thick film, as they are on a well-painted surface. For, although the red penetrates deeper, it is finally scattered or reflected to practically the same degree as the blue. But if the film is thin or the particles are widely spaced, considerably more red than blue finds its way through the film. Suppose such a film covers a black surface, then the excess of red is absorbed by the surface and the film-covered surface has a blue-gray appearance.¹ A white pigment containing no grains less than 2 μ in diameter under the same conditions produces a neutral gray. In certain mixed pigments these effects of size of grain are very pronounced. (See Sections XI and XIV.)

Samples of the various white pigments were tested over a black surface. All of them gave more or less bluish grays, dependent upon the amount of very fine grains which they contained. Search was then made amongst a large assortment of chemicals—in the form of white powders—to find one which would produce over black a true neutral gray, and which would also be a fairly “strong” white. A sample of lead sulfate was found satisfactory. Its grains ranged between 2 and 5 μ . This sample may be called a “true” white.

Zinc oxide has a high refractive index and absorbs no color except in the extreme violet. It can be produced in clear grains

¹ A blue of considerable brilliancy (blue 25 parts, neutral gray 75 parts) can be produced by pressing a film of very fine-grain zinc oxide paste very thin, under a cover glass on a glass slip blackened on the under side.

of various sizes by the dry processes. The burning vapor of metallic zinc produces an exceedingly fine-grain oxide—grains much less than $1\ \mu$ in diameter. Reheating causes growth of some particles at the expense of others, with the ultimate development of a definitely crystallin powder.

The burning of zinc blende produces a powdery oxide less even-grained than that from metallic zinc. If the blende contains a few per cent of lead the pigment after reheating may contain a large proportion of particles more than $2\ \mu$ in diameter, lacking definite crystallinity, and low in refraction.

Most of the zinc-oxide pastes contain enough material finer than $1\ \mu$ to add considerable blue color, due to scattering to paints in which they are mixed, and to reduce somewhat the hiding power of the paints.

White lead is a definitely crystallin material even less light-absorbing than zinc oxide, and of about the same refractive index. That made by the Dutch process is considerably coarser than zinc oxide. Greater hiding power would be secured from a finer-grain powder, such as may be produced by precipitation.

Basic-sulfate white lead has lower refraction than white lead or zinc oxide, and is about as fine as zinc oxide.

Lithopone contains grains of various refractive indices and sizes. Reference to the detailed description of a sample is necessary to the understanding of its properties.

XI. EFFECTS OF MIXING BLACK AND WHITE PIGMENTS.

The true white previously described (see Section X) was mixed with several black pigments to produce grays. Graphite and lampblack produced neutral grays, but ivory black and magnetic-oxide black produced slightly brownish (orange) grays. The finest-grain French-process zinc oxides, with graphite and lampblack, produced very blue grays; some contained as much as 10 per cent blue. American-process zinc oxides and other commercial white pigments gave grays containing 2 to 5 per cent blue. Thus, in mixture with black, these fine-grain whites give blue grays which are, however, less blue than may be produced over a background of black. (See Section X.) The orange tinge of grains of ivory black and magnetic-oxide black may neutralize the blue which white pig-

ments produce in mixtures, so that neutral grays can be made. A test was made to determine how much blue would be required to be mixed with a true white, to give with ivory black a blue-gray like that produced by graphite and White-Seal zinc oxide. The blue pigments used were ultramarine, Prussian blue, and true cobalt blue. It was found that a bright blue, corresponding to 70 to 80 per cent blue, was required.

XII. COLORED PIGMENTS IN MIXTURES.

Only in the form of pastes are mixtures considered in this section. The colors of the same or similar pigments mixed dry are discussed in Section XV.

Intermediate Hues.—So far as color absorption alone, without regard to refractive index and size of grain, is concerned, the theory of the production of intermediate hues is well known. In these cases transmitted light only has been considered. For example, a thin film of Prussian-blue paint is blue by transmitted light; likewise, a film containing powdered sodium chromate is yellow. Green is transmitted by the two films superposed or a film made by mixing. But a film of the mixture over a black background scarcely reflects any light at all, except the small amount from the surface of the vehicle. If lemon chrome, which in dry powder is nearly the same yellow as sodium chromate, is substituted for the sodium chromate, then a fairly bright green is diffusely reflected, and much less transmitted. The lemon chrome, because of its high refractive index, reflects diffusely the green light transmitted by superposed grains of the two pigments in the mixture. Hydrous sodium chromate and Prussian blue, on the other hand, have nearly the refractive index of the vehicle. The quality of the green produced by such mixing depends upon all the fundamental optical properties of the pigment grains. In the usual case, the intermediate hue is considerably absorbed by both substances, thus rendering impossible the production of a very bright color, and making fineness of grain essential. If the grains of the substance having highest refraction are of optimum size for diffusing light, then the other substance may profitably be much finer, for example, lemon chrome yellow with very fine Prussian blue. Or it may be best to have both pigments very fine and accomplish the diffusion by admixing an effective white pigment. In some cases the colored substances

form very thin films upon suitably sized grains of either "strong" or "weak" white pigments.¹ In other cases films of one pigment are precipitated upon the other.² This last is a most efficient method of using the precipitated substance, but only such substances as are very strongly colored can be thus used.

In case both substances are highly transparent to wavelengths producing the intermediate hue, the size of grain is of little importance in the production of a full hue, but it is of the same importance as usual in relation to diffusing power. For example, a green of great intensity can be obtained from lemon chrome of usual grain and bluish verdigris, although the verdigris is coarse grained.

In any case, grains near the exposed surface of the paint film will reflect some white light and some light which has traversed grains of only one color. The result is a hue of slightly decreased purity.

Purple is considered an intermediate hue between red and violet, in the sense that if pigment grains transmit and diffuse both red and violet or red and blue in proper proportions, the resulting color is purple. Very few highly refracting substances suitable for pigments possess such transparency except in a slight degree. Therefore, only dark purples are produced by mixing two pigments, one of which is predominantly red and the other predominantly violet or blue. But by adding a strong white to such a mixture the hue can be considerably intensified. (See Section XIV.)

Mention has already been made of the scattered blue produced by mixing a very fine-grain white with black or other dark pigment. This blue can be made available in the production of purple when certain reds are used.

XIII. HUES MODIFIED BY ADMIXTURE OF BLACK.

A Simple Wet Pigment Mixed with Black.—The chief effect of mixing black with a pigment having one constituent, is to decrease the brightness by decreasing both the white and the colored components of the diffused light, but marked changes in hue may result. Hue changes are chiefly the result of three

¹ Some of the most brilliant chrome greens.

² Para red upon red lead.

tendencies, namely, migration of the hue toward (1) the violet end of the spectrum, (2) the absorption band, and (3) the color most refracted. The combined effects of these tendencies are shown in Fig. 7.

1. All pigments reflect diffusely colors representing a considerable range of wave-lengths. Admixture of black diminishes the physical intensity of the whole range of wave-lengths to the same degree, yet the apparent (physiological) intensity of longer wave-lengths is diminished more than that of shorter wave-lengths. Thus the resulting color differs from the original in hue as well as in brightness.¹ The effect is most noticeable in the part of the spectrum, yellow, for which the sensibility of the eye to differences in hue is greatest. A yellow pigment greatly darkened tends to appear dark greenish yellow, and a darkened yellowish green tends to appear bluish green.

2. Black grains interposed among colored grains intercept light which would otherwise traverse more colored grains, before being returned through the surface of the mass. Thus the emergent light is less completely robbed of the wave lengths near the absorption band, than if the black grains were not present. The tendency toward change of hue is most pronounced in fine-grain pigments, especially if absorption increases gradually toward one end only of the spectrum.² For example, chrome yellow absorbs gradually through the blue and violet, so that when mixed with black it becomes more greenish than the Purkinje effect alone would account for.

3. High refraction favors diffuse reflection; therefore, that component of color for which pigment grains have the highest refractive index is diffusely reflected out of the mass of grains, after traversing a shorter average path than that component which is less refracted. Thus, fewer admixed black grains will

¹ Besides this (the Purkinje effect) there is probably another physiological effect even more pronounced which has led to such color names as olive-green, calla green, etc. These are really only dark yellows (Ridgway, Plates IV, V).

If the spectra from a diffraction grating are observed through a Wratten filter No. 77—or 77 and 58—which absorbs a narrow band in the middle of the yellow, the brightest spectra show bright yellow near the absorption band grading into green. But in the fainter spectra green encroaches upon the yellow so that in the faintest spectra only green is seen.

Four sets of yellow screens were matched with spectral colors by means of two microscopes with rotating nicols and a comparison eye-piece. After darkening about 95 per cent no change of hue of the screens of more than $2 \mu\mu$ toward the green was observed. Thus the Purkinje effect in Ridgway's colors seems to be negligible.

² Two absorption bands complicate the application of the principle, but do not affect it otherwise.

be encountered by the former, and it will be correspondingly less diminished in intensity. This effect is small compared with the two just described, and is negligible in most cases.

Mixed Pigment plus Black.—In addition to the foregoing tendencies another of importance must be considered. If a paint contains two pigments—in separate grains—which differ markedly in hue, then adding black will cause the brighter hue to tend to dominate. For example, orange made from yellow and red will when darkened with black tend to become like a darkened yellow. This tendency may be about balanced by the tendency of high refraction to favor diffuse reflection, as when zinc yellow and verdigris are mixed with black.

XIV. COLOR MODIFIED BY ADMIXTURE OF WHITE PIGMENT.

Adding white increases the brightness of a paint, but there may be notable changes in hue also.

The chief brightening effects (see Fig. 3) can be discussed best if the original paint is assumed to contain but one pigment. If the paint is a tint or nearly full color, the resulting color will be a tint having intermediate brightness. If the paint is a dark or intermediate shade then the diffusing power and absorption (or transmission) characteristics of the pigment must be considered.

Weak Diffusing Power.—If the transmission is high, the first small portions of white added diffuse the color and thus increase the percentage of color to a high maximum; further additions of white produce tints intermediate between the maximum color and white. Examples: verdigris, rose madder and ultramarine. If the transmission is moderate or low the effects are similar, except that the maximum color is duller. Examples: burnt sienna, Dutch pink, permanent violet.

Strong Diffusing Power.—If transmission is high, even the first portions of white added will dilute the color. If transmission is moderate or low, the first white added will tend to increase the color but the amount of such increase will not be large, especially if the pigment does not contain small grains. Examples: vermilion, chromic oxide, Indian red, bright red oxide, Venetian red. (See Fig. 3.)

The hue changes produced by adding white to a colored

one-pigment paint depend upon the fineness of the white, as well as upon the properties of the colored pigment. The blue and violet light scattered and differentially reflected under certain conditions by fine-grain white pigments produces corresponding changes in hue when mixed with the color from a colored pigment. Although there are many conditions under which this blue appears,¹ it is striking in case of colored pigments only when the original color is some tone of red, preferably a dark red shade produced by a pigment having strong primary diffusing power. In this case the blue, which is a considerable fraction of the total light diffused, combined with the red gives purple. Indian red with White-Seal zinc oxide gives a decided purple, while with a coarse-grain white the lightened color inclines toward orange. Even light tints of alizarin lake, vermilion and rose madder are quite noticeably different when made with the whites just mentioned. (See Fig. 7.)

Strongly diffusing white grains among colored grains cause a decrease in the distance which light traverses through the colored grains; thus there is a tendency for the hue of a colored paint to migrate toward the absorption band of the pigment when white is added. (See Fig. 7.) The amount and rate of the migration compared with the brightening depend chiefly upon the fineness and the transmitting properties of the colored pigment. In general the tendency is slight for coarse-grain pigments. A very fine-grain pigment having moderate transparency, such as Prussian blue, will show decided migration. One with fine grain, high transmission and a very indefinite absorption boundary will show a large migration; for example, crystallin lemon chrome yellow. Zinc chromate and chrome yellow when not crystallin may be so coarse grained as not to show appreciable change of hue when tinted out.

Mixed Pigment.—In general the hue of a mixed pigment or paint cannot be so greatly intensified (brightened) by the addition of white as the hue of a simple pigment; otherwise the brightening effects of added white are essentially the same in the two cases.

The migration of the hue of a mixed paint caused by adding a true white depends upon the position of the absorption bands of the colored pigments. If the absorption bands are

¹ See Section X for theory.

on opposite sides of the hue, as in green and purple, the tendencies to migrate toward the two bands will be more or less balanced. If the bands are on the same side of the hue, as when orange is produced by mixing red and yellow, the tendency to migrate toward the absorption band will be greater than for either pigment alone. Some red pigments transmit enough violet to affect appreciably the migration of hue of a mixed orange. An uneven-grain pigment with a very gradual absorption gradient will behave like the mixed red and yellow.

XV. DIFFERENCES IN COLOR BETWEEN WET AND DRY COLORED PIGMENTS.

The difference in refractive index between air and paint vehicles is so great that the diffusing power of a pigment is much less wet than dry. On account of high primary diffusing power (see Section IV) all dry colored pigments diffuse notable amounts of white light. For this reason among others, their colors are impure. Wetting greatly decreases both primary and secondary diffusing power, and thus increases the purity of color and decreases its brightness. Pigments having about the refractive index of the paint vehicle are more greatly affected than those having high refractive index. Decrease in brightness may be accompanied by an increase or decrease in the percentage of color (hue), and also by displacement of the hue. Size and constants of absorption as well as refractive index of the component grains must be considered in a further discussion of this topic.

One Constituent.—In the case of a simple pigment, wetting causes the hue to be displaced away from the absorption band because the lessened diffusive power permits deeper penetration and greater absorption. (See Section V.)

Factors which favor great increase in the percentage of color on wetting are moderate to weak absorption, fine grain, moderate to high refractive index. Such a pigment when dry will give a bright tint, when wet it will still have sufficient secondary diffusing power to prevent much absorption of the characteristic hue. Other favorable factors remaining the same, it is evident that there is an optimum refractive index, which is probably less than 2.0 and greater than 1.75. It is

essential that absorption be not strong. A number of colored substances showing such change are shown in Fig. 5.

Low refractive index, strong absorption, and coarse grain favor a decrease in the percentage of color on wetting, but the effect is shown even with fine-grain highly refracting substances if absorption is excessive, for example, Indian red.

Changes in brightness due to wetting depend chiefly upon the relation between the absorption gradient and the diffusing power. High refractive index and optimum fineness of grain are necessary to prevent large loss of brightness when a pigment having a gentle absorption gradient is wet. On the other hand if the absorption gradient is steep, loss of brightness on wetting will be far less dependent upon size of grain and refractive index. Examples of pigments in which such change is small are zinc yellow, lemon chrome yellow, red lead, and emerald green.

Migration of hue caused by wetting simple pigments is usually slight. Low refraction, fineness of grain and gentle absorption gradient favor such change.

Mixed Pigment.—The darkening and change in intensity of the colored component of a mixed pigment caused by wetting can be largely inferred from what has preceded. The migration of hue, which may be large, needs a little more consideration. Red and yellow mixed dry produce a somewhat dull orange. Wetting causes a pronounced displacement of the hue toward red. A large part of the yellow green diffused by the dry yellow pigment is absorbed by the red pigment when deeper penetration is permitted by the wetting. In case of a mixed green, wetting causes about equally increased absorption of yellow and blue.

Red and blue mixed wet produce so dark a purple that its hue can scarcely be determined. The addition of a little white increases the color. The mixture when dry has in general a different hue, owing chiefly to the tendency for the hue to be displaced toward that of the more strongly diffusing colored pigment.

A very notable effect of strong secondary diffusion, especially in dry mixed pigments, is color due to juxtaposition of colored grains at the surface of the pigment mass. Each grain diffuses light of its own color besides light which may have traversed

grains of another color. Much of the purple produced from red and blue originates thus. A neutral gray diffusing more than 25 per cent of white can be made from dry red, green and blue pigments.

XVI. METHODS.

Some pigments contain many composite grains which do not become disaggregated when spread in a film of paint. Such grains vary from compact masses to masses which consist of nearly spherical component grains joined so as to have a large amount of pore space. The term "size of grain" when grains are porous might better take definite account of size of single grains and size of composite grains, and number or volume of each. Fresh oil pastes should be used when possible in testing grain, for these contain the pigment in as nearly as possible the same state of aggregation that it will have when spread. Of course some pigments can be mounted on a microscope slide in practically the same state of fineness whether dry or wet, but others can not.

Mounting for microscope study should not be done in a mobile liquid, for the finer grains tend to concentrate near one edge of the cover glass, and even loose aggregates from a dry pigment are broken up in it with great difficulty. A very viscous, sticky mounting material can be made by melting together about equal parts of rosin and camphor. The viscosity of this mixture can be lowered greatly by slight heating. Thick Canada balsam may be used less satisfactorily. The object of mounting is to obtain a film as thin as the largest pigment grains will permit, with the grains separated sufficiently for counting. This can be accomplished by mixing a very little of the mounting material and pigment under a small cover glass which is given a rotary and sliding motion by firm pressure. There is little possibility of crushing grains by this means.

Measurements of optical constants were made by means of the petrographic microscope and standard refractive immersion media.

XVII. OPTICAL PROPERTIES IN DETAIL.

Graphite.—(See Section IX.) Graphite cleaves readily and forms in plates parallel to the cleavage, so that the optical properties measurable on cleavage flakes are chiefly responsible

for its behavior as a pigment. Microscopic flakes thin enough to transmit grayish light have been prepared. Its refractive index ω is about 3, and its reflecting power high (about 37 per cent).¹

Ivory Black, Bone Black, Drop Black, etc.—(See Section IX.) In charred bones a small amount of dark carbonaceous matter is held in the most minute subdivision throughout a large amount of calcium phosphate. Grains $5\ \mu$ in diameter transmit an appreciable brownish color and appear practically homogeneous optically. Their apparent refractive index, when their pores are filled with oil, ranges from about 1.65 to 1.70. Thus, the desirable characteristics of slight diffusing power and effective absorbing power are combined.

Basic-Carbonate White Lead.—Basic-carbonate white lead is a definitely crystallized substance. Individual grains seen in several samples were tabular (perhaps twice as broad as thick), and hexagonal in general outline.² The two chief refractive indices³ are $\omega=2.09$, $\epsilon=1.94$. In ground samples of this pigment relatively few grains, except possibly the smaller, are single crystals; most are made up of several small crystals or fragments firmly intergrown in various orientations. Such grains are more effective diffusers of light than those of equal size which are single crystals. About 40 per cent by calculated volume of each of four samples studied, consists of grains less than $2\ \mu$ in diameter and about 90 per cent less than $5\ \mu$. Several per cent of the "normal" lead carbonate is often present in commercial white leads. It is easily identifiable microscopically, because it occurs in clear crystal fragments of relatively large size which, as usually oriented, have much stronger double refraction than the basic carbonate. Also, its least index of refraction is only 1.80, and it has a strong tendency to appear in negatively elongated prismatic grains. Tables of the basic carbonate seen edgewise have positive elongation. The highest refractive index of the normal carbonate is 2.08.

¹ Wartemberg, *Ber. dent. phys. Ges.*, Vol. 12, p. 105 (1910); also Zakrzewski, *Anz. Akad. Miss. Krak.* 1910, p. 122.

² These crystals when studied more minutely were seen to be a rhombohedron and base. From some of them a clear uniaxial negative interference figure was obtained. In these respects they correspond to the mineral hydrocerusite. L. F. Hawley, *Journal of Physical Chemistry*, Vol. 10, p. 654 (1906), proved that white lead is a definite compound by a study of its solubility. The formula thus obtained agrees with hydrocerusite.

³ From the natural mineral, hydrocerusite, E. S. Larsen obtained $\omega=2.07$ (unpublished).

Basic-Sulfate White Lead.—Basic-sulfate white lead is not definitely crystalline. It consists of minute spherules which are themselves firm aggregates of much more minute particles. The single refractive index of the sample studied was 1.93. It is probable that samples will differ slightly in refraction. From the structure of the grains it is inferred that they have a much rougher surface than the crystal grains of zinc white. Yet owing to the minuteness of the grains, this roughness probably does not very materially affect the diffusive power of the pigment. This sample was almost identical in fineness with white zinc, but it contained larger, loosely aggregated composite grains. Such grains, however, must have nearly as great diffusive power as if distributed singly.

Lithopone.—The single sample of lithopone studied did not contain identifiable crystals although there was doubly refracting material present. Pronounced lack of homogeneity was brought out by differences of refraction in single grains and among different grains. Doubtless such lack of homogeneity extends to the sub-microscopic magnitudes. The term "grain" here used means, then, fragments produced by pulverizing firmly aggregated material. In this sample about 70 per cent, by calculated volume, of the grains were smaller than $2\ \mu$. Only a small percentage were larger than $4\ \mu$ or smaller than $0.6\ \mu$. Few grains larger than $1.5\ \mu$ had uniformity of refraction. Portions of the sample were examined in liquids of measured refractive indices, and the indicated percentages by volume of the sample which were higher in refraction than the liquid were estimated roughly as follows: 1.70, 99 per cent; 1.74, 97 per cent; 1.78, 85 per cent; 1.84, 65 per cent; 1.90, 20 per cent; 2.10, 5 per cent; 2.25, 1 per cent.

Lithopone is prepared by heating and quenching a simultaneously precipitated mixture of zinc sulfide and barium sulfate—a process which might conceivably give so intimate a mixture that it would appear microscopically homogeneous. But if consideration is given to the very great difference between these two substances in tendency to crystallize from aqueous solution, then the graded heterogeneity observed may be accounted for in something like the following way: Within the mass of intimately mixed precipitates, nuclei of barium-sulfate crystals begin to enlarge into more or less interlocking groups,

the groups enclosing some, pushing aside other zinc sulfide. This process is halted before many single crystals reach a size greater than about 0.3μ , but groups with enmeshed zinc sulfide may have a diameter of about 1.5μ . Heating would expel the enclosed water, and cause the zinc sulfide to crystallize. An aggregate formed of two substances by the adherence of grains less than about 0.3μ in diameter will have an apparent refractive index determined by the proportions of the two substances. The refractive index of crystallin barium sulfate is 1.66, and of crystallin zinc sulfide is 2.37. These values are about the limits of the refractive indices of the grains of lithopone.

Zinc Oxide.—Zinc oxide (see Section X), when pure and of not too fine grain contains stout prisms with parallel extinction, positive elongation, $\omega = 2.00$, $\epsilon = 2.02$. The presence of even a few per cent of lead prevents to a large extent the growth of crystals, but does not hinder during reheating the process of aggregation of fine particles into dense masses 3 to 5μ in diameter. These may have a refractive index as low as 1.94.

Harrison Red.—Harrison red consists of minute crystals, probably orthorhombic, rounded grains and stout prisms about 1μ in diameter; elongation negative; $\alpha_{Na} = 1.60$, $\beta_{Na} =$ about 2.1_{Na} , $\gamma = 2.25_{Li} = 2.33_{Na}$. The optical dispersion of γ is very high from the red to the green. Pleochroism pronounced, α orange, β and γ deep red. Grains are practically opaque to green and blue but transmit some violet. The violet becomes very evident if a thin film containing crystals dispersed sparsely in oil is viewed by transmitted light, especially if this color is compared with the orange red diffused by the film.¹ Heated with large excess of linseed oil the crystals dissolve to an orange-colored liquid, which deposits spicular crystals on cooling. These crystals have the same color, pleochroism and elongation as the original ones. It may be noted, however, that on account of the pleochroism with respect to shape the coloring power of the spicular crystals would not be as great as that of the nearly equi-dimensional original crystals. Also, the diffusing power of the spicular crystals would be very considerably less on account of birefringence with respect to shape. (See Section VII.)

Vermilion.—Vermilion (HgS) varies somewhat in color

¹ The refractive index for violet must be considerably less than for red to account for this difference (compare with ultramarine).

owing to differences in grain. Its refractive indices are very high, $\omega_{Li}=2.81$, $\epsilon_{Li}=3.14$.

Indian Red.—Indian red consists of very small hematite (see scarlet oxide) crystals, mostly from 0.5 to 1.0 μ , which may be aggregated into rough grains up to about 5 μ , $\omega_{Li}=3.01$, $\epsilon_{Li}=2.78$.

Scarlet Oxide.—Scarlet oxide or jewelers' rouge—hematite in smaller grains than Indian red—color brighter and more nearly orange than Indian red. Grains of hematite 3 μ in diameter would have such low transmission that a pigment consisting of them would be a dark gray with little color. Films of hematite may be thin enough to transmit a light orange-yellow color. Such plates transmit all colors, but blue and violet noticeably less than the others. Plates a little thicker are orange, and transmit little between 450 and 500 $\mu\mu$, but from 450 to 400 $\mu\mu$ transmission seems to increase.¹ It is evident that colors ranging from orange yellow to dark red or purplish can be obtained from crystalline hematite if proper means of diffusing the color are furnished. Yellowish colors could be obtained only by means which would insure complete diffusion before the light had traversed a total thickness of the hematite greater than about 0.1 μ .

Alizarin Lake (Crimson).—The isotropic base with the coloring matter has a variable, low refractive index—about 1.70 for red. Thus the diffusing power is low. The sample examined contained a small percentage of grains about 10 μ in diameter. Such grains transmit very little between wave lengths 480 and 550 $\mu\mu$, and even red is slightly absorbed. Violet is not strongly absorbed. When tinted out with white the presence of the large grains causes dullness.

Scarlet Lead Chromate.—The single sample of scarlet lead chromate examined consisted of beautiful rectangular tabular crystals 2 to 5 μ thick and from 3 to 10 μ in other dimensions. The extinction is parallel, γ vibrates normal to the plates and α parallel to the elongation. α is orange-yellow γ and β are orange-red. $\alpha_{Na}=2.42\pm0.01$, $\beta=2.57_{Li}$ or 2.7_{Na} , $\gamma_{Li}>2.57<2.62$. The symmetry is probably orthorhombic.

¹ These observations were made on flakes of hematite in aventurine feldspar furnished by Mr. Olaf Andersen of the Geophysical Laboratory. He calculates the thickness of yellow plates as 0.1 μ , *American Journal of Science*, Vol. 40, p. 370 (1915).

This even-grain, coarse-grain sample when mixed with oil had a pure, slightly darkened color—between *5 h* and *5 i* of Ridgway's scale. It maintained its hue and purity when darkened with ivory black. When brightened with white it maintained its hue but produced slightly dull tints—*5' d* and *5' f*.

Some of the dry pigment was ground in oil until its hue changed to near orange—*9 h*. It was now very uneven grained, many grains of the original size remained and a small percentage of the volume was as fine as $0.5\ \mu$. It still tinted out dull on account of the presence of the large grains, and the small grains caused the hue to migrate a good deal when it was darkened with black—to $13\ \mu$.

Red Lead.—Red lead is known in three different forms, as follows:

1. The mineral "minium" occurs in needle-like crystals with parallel extinction, which are strongly pleochroic from yellow to red.

2. Scaly or irregular grains which are crystal units without definite outlines, are formed commercially by oxidizing litharge flakes. As oxidation proceeds from points on the surface of the flakes the crystals of red lead replace the litharge. Imperfect oxidation can be detected by observing the optical properties of the product (see litharge). These grains of red lead are strongly pleochroic, show anomalous green interference colors, have very slight birefringence and a refractive index of 2.42_{Li} and 2.5_{Na} . Some samples which are relatively coarse grained, 20 to $50\ \mu$ diameter, are almost completely oxidized, while others which contain relatively small amounts of grains larger than $20\ \mu$, contain more than 10 per cent of unoxidized material.¹

3. Red lead, which shows almost no crystalline structure and appears as friable aggregates of particles which are exceedingly small, is prepared from lead monoxide derived from lead carbonates.

The color of these several products varies. The third is the lightest. In the first and second, size and shape of grain are factors determining color—coarse-grain material is darker or redder except when poorly oxidized.

¹ A series of analyzed samples was furnished for these studies by P. H. Walker of the U. S. Bureau of Standards.

Burnt Sienna.—Burnt sienna is very uneven grained, but contains much very fine material. It shows no evidence of crystallinity, grains have variable, moderate refractive index,—around 1.85,—and are fairly transparent to red, orange and yellow. One effect of its diversity of grain is worthy of notice. White, added gradually, first intensifies the color, then because of the large grains the shades become dull as the white acts as a diluent.

Massicot in its commercial form is a yellowish, powdery form of PbO. Natural yellow crystals of PbO have been known for many years as massicot. The crystals are orthorhombic scales or thin plates, faintly pleochroic with γ most strongly absorbed, $\alpha_{Li}=2.51$, $\beta_{Li}=2.61$, $\gamma_{Li}=2.71$. PbO which has crystallized from fusion in dull orange flakes is known commercially as *litharge*. Microscopical examination shows the flakes to consist largely of yellow massicot. The orange color is due to reddish streaks, of another, tetragonal, crystalline form of PbO for which no definite name exists, although it has been called red litharge. It is not noticeably pleochroic, $\omega_{Li}=2.66$, $\epsilon_{Li}=2.53$.¹

Chrome Orange.—Not enough samples of this pigment have been studied to yield definite results. The grains are not well defined crystals as in the case of the three other lead chromates described, and the pigment is not essentially a mixture of such crystals. The refractive indices are intermediate between those of the scarlet chromate and chrome yellow medium.

Barium Chromate.—No distinct crystals were seen in the one sample examined. Particles 2 to 5 μ in diameter consist of globules or lumps with irregular double refraction, $n=1.94$ –1.98.

Cadmium Yellow.—See *American Journal Science*, Vol. 34, pp. 365–387.

Zinc Yellow.—One sample examined appeared like barium chromate, but n is lower, $n=1.84$ –1.90.

Lemon-Chrome Yellow.—Only one out of six samples of this pigment from various sources was not distinctly crystalline.

¹ The relation of these forms in nature has been studied by E. S. Larsen, Jr., *Am. Min.*, Vol. 2, p. 18 (1917). These refractive indices were partly measured on crystals made by L. H. Adams of the Geophysical Laboratory.

This one consisted of formless lumps and fine grains having a refractive index of 2.0 to 2.1 for yellow.¹ It was among the yellowest—22. The other samples were composed largely of prismatic or rounded grains $1\ \mu$ or less in diameter, extinction parallel, elongation γ ; refractive indices $\text{Na} : \alpha = 2.10\text{--}2.12$, $\beta = 2.2(1)$, $\gamma = 2.38\text{--}2.43$. The crystals are probably orthorhombic, and are optically related to lead sulfate, though differently elongated. The problem of their exact relation to lead sulfate requires a study of conditions of precipitation in relation to optical (and possibly other physical) properties and composition.

Chrome Yellow Medium.—Samples from four sources all consisted essentially of prismatic crystals mostly less than $0.7\ \mu$ in diameter and 2 to $6\ \mu$ long. The crystals extinguish parallel, have positive elongation, and refractive indices $\gamma\ 650\ \mu\mu = 2.49$, $\alpha\ 620\ \mu\mu < 2.31$. Analysis furnished by P. H. Walker showed 5 to 11 per cent excess PbO over PbCrO_4 .

Chromic Oxide.—Several samples were examined. All consisted of porous lumps in which individual particles could not be distinguished. The most compact material showed considerable transparency, even for red and orange, and noticeable absorption in the green. These characteristics account for the dullness of its color, especially in mixtures. Its refractive index is high, but could not be found accurately. The value $n_{Li} = 2.5$ was obtained. Probably this is about the value for green and violet also, for in the hydrated oxide dispersion is very low.

Chromic Oxide ("transparent").—This is probably a hydrated oxide without crystallinity. Lumps $20\ \mu$ in diameter are dull greenish with absorbing properties similar to the anhydrous oxide but much weaker. $n = 1.625\text{--}1.645$ for yellow and is practically the same for other colors.

Verdigris.—Irregular crystal fragments, pleochroic from lighter blue-green, γ , to deeper green-blue, α ; $\alpha = 1.53$, $\gamma = 1.56$; $2\ V$ very large, and the bisectrices strongly dispersed. Grains $30\ \mu$ in diameter transmit considerably throughout the spectrum.

¹ Analyses furnished by P. H. Walker showed 26.98 per cent lead sulfate, and for one of the crystallin samples 35.02 per cent. This was not present in separate crystals.

Cobalt Blue (cobalt aluminate).—Grains vary in depth of color; those most deeply colored have the highest refractive index, which for blue is 1.74, for red a little > 1.78 , and for green < 1.73 . Grains $10\ \mu$ in diameter are practically opaque to wave-lengths between 560 and $610\ \mu\mu$. Wave-lengths in the red longer than $650\ \mu\mu$, and blue and violet, are freely transmitted. Considerable colorless isotropic material of refractive index about 1.70 was found adherent to and mixed with the colored grains. The refractive index of the colored grains is about what would be expected of crystalline $\text{CoO} \cdot \text{Al}_2\text{O}_3$, that is, cobalt spinel.¹

Ultramarine.—The grain of ultramarine is about that of Dutch white lead. Particles of medium size are pale blue and isotropic. Their refractive indices cannot be measured for sodium light because they are opaque to it. They are fairly transparent for red light, for which the refractive index is about 1.63 for Li-light. Measured in green light wave-length $520\ \mu\mu$ the refractive index is 1.51; in the violet light at $450\ \mu\mu$ it is 1.535. Thus the dispersion is anomalous, because the refractive indices are lower for green and violet than for red.²

Permanent Violet, a manganese compound.—Crystals probably orthorhombic $4\text{--}8\ \mu$ in diameter, in flat double pyramids with corners truncated. β , perpendicular to plane of flattening, $\approx$ about 1.72 for violet; α , parallel to greatest elongation, $\approx$ 1.64 orange, 1.65 green, 1.67 violet; $\gamma = 1.79$ orange, 1.73 green, 1.75 violet. $2V$ is about 45° . γ and β are violet-red, α is colorless or light gray. If α were perpendicular to the plane of flattening the pigment would have more color, perhaps 25 per cent, and more diffusing power. The sample examined contained some ultramarine.

The Lakes.—The colorless bases which receive the coloring matter have refractive indices which are low and variable, 1.58–1.72 usually. The coloring matter slightly affects the refractive index. The particles of the lake vary from very

¹ See J. A. Hedvall, Arkiv, Kem. Min. Geol., Vol. 5, No. 16 (1914).

² Small amounts of lighter colored materials are intimately associated with the ultramarine. These do not vary in refraction like the ultramarine, but they have when in a refractive liquid practically the same apparent refraction as ultramarine in ordinary light. Thus, although the heterogeneity of the material is not apparent in ordinary light, it manifests itself at once in green or red light and makes refraction determinations difficult.

coarse to very fine. Lakes with coarse to very fine particles, and refractive index about 1.60, are very transparent in thin films with oil, and are thus good as glazing colors. Fine-grain lakes having refractive indices 1.65-1.72 are only semi-transparent in such films and thus are not so good as glazing colors. The film, if made between glass slips, may diffuse a noticeably different color from what it transmits.

FIG. 1.

Each apex in Fig. 1 represents 100 per cent of either white, black or full color. The percentage of each of these decreases regularly to 0 at the opposite side. Tints containing no black—along *CW*—may be called clear tints, and shades containing no white—along *CB*—may be called pure shades. These terms may be applied in practice to tints and shades containing respectively a little black or white, which would be overlooked in a casual examination. Dull (broken) colors occur over the interior of the triangle, neutral grays along *WB*, and colored grays adjacent to *WB*.

FIG. 2.

Fig. 2 shows the positions of the Ridgway colors. The subscript *R* is used to indicate that the colors are made up, not of theoretically perfect black, white, and full color, but of standards specified by Ridgway. When color analyses of these standards are available it will be found that for each of the standard hues (full colors) and their modifications by black, white and gray the lettered positions on a triangle representing the analyses will be different. The symbols for intersections not marked can be inferred.

FIGS. 3 TO 7.

The curves in these figures are selected from a larger number of curves to illustrate typical conditions. Different samples of the same pigment give the same type of curve, with rare exceptions, but not necessarily the same curve. Some substances which are not ordinarily used as pigments have been studied because of their illustrative value.

FIG. 3.

White pigment added to colored paints. (See Section XIV.) Increasing white causes changes shown by arrows. Some changes follow the boundaries *B* to *C* to *W* (true cobalt blue), or *C* to *W* (cadmium orange, zinc yellow). A very fine-grain white produces with Indian red or lamp-black the curves "a", but a white containing no very fine grains produces the curves "b".

FIG. 4.

Black pigment added to colored paints. (See Section XIII.) A non-diffusing black pigment like ivory black when added to a paint or moistened powder consisting of a single kind of grains and having a certain proportion of white in its diffused color should diminish the white and color almost proportionately. That is, the curve of darkening should be a nearly straight line across an ideal triangle, joining the position of the color with a very dark gray (containing about 4 per cent white). On the triangle here shown the true proportions of white and color are not exactly represented, therefore the curves for the single pigments may not be of true form. The tints produced by mixing color with a strongly diffusing white must, when gradually modified by admixed black, lose color much faster than they lose white, because white grains assist largely in diffusing the color transmitted by colored grains. The three such curves on the diagram are concave in the proper direction, but the one representing white plus yellow lake can not be an ideal curve, for white appears to increase during the first additions of black. The fault is not in the color comparisons but in the standards. The curvature for a strongly diffusing colored pigment is less than for one which is weakly diffusing. (Compare vermilion and alizarine lake.)

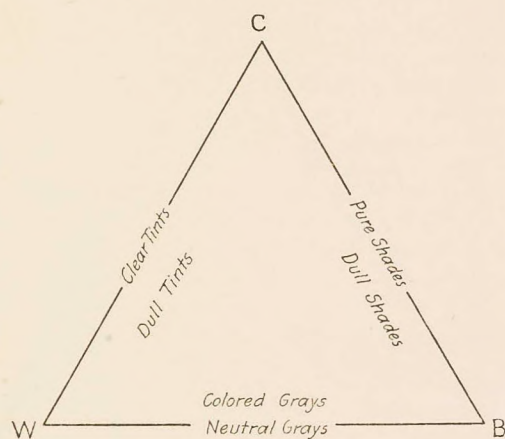


FIG. 1.

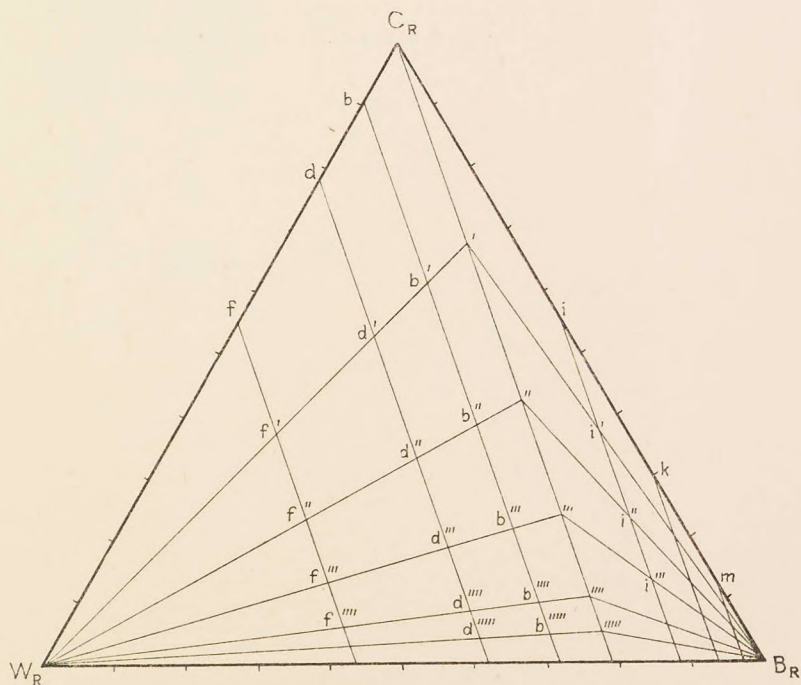


FIG. 2.

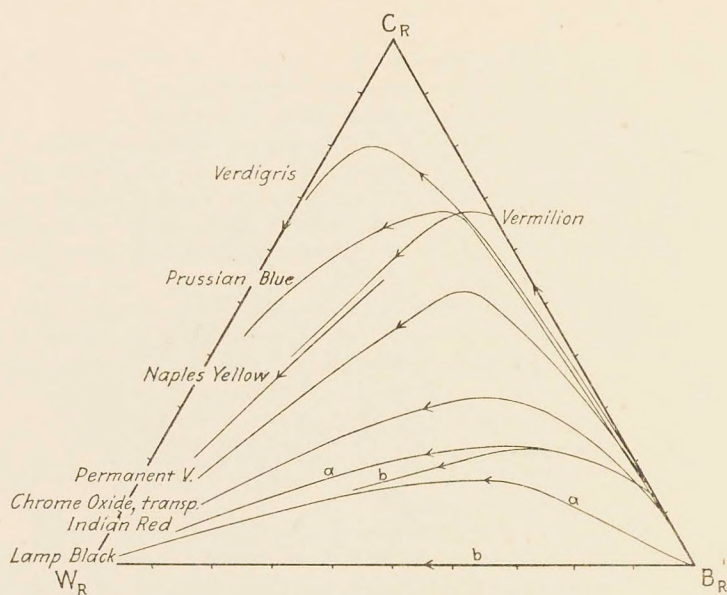


FIG. 3. (see p. 30).

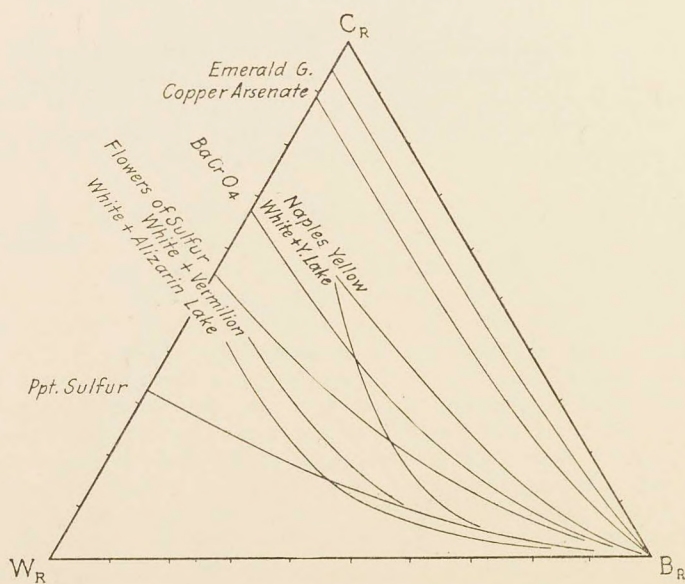


FIG. 4. (see p. 30).

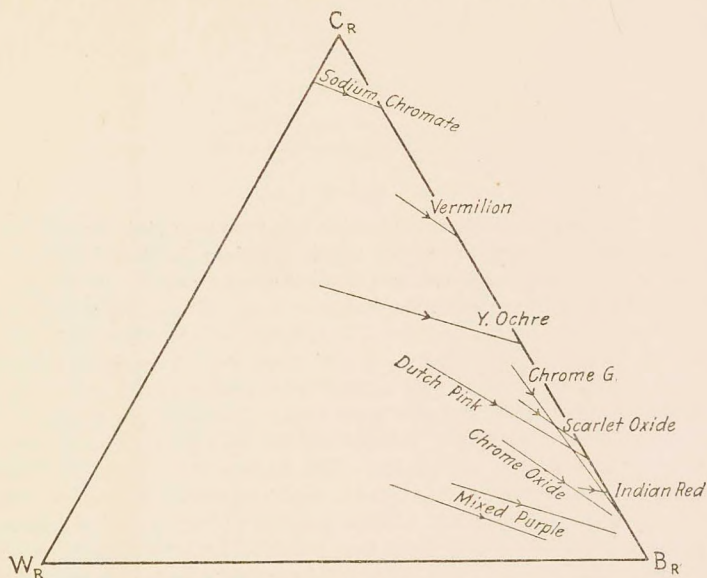


FIG. 5.—Wetting (mixing with oil) causes the color of these pigments to become more nearly pure but less nearly full.

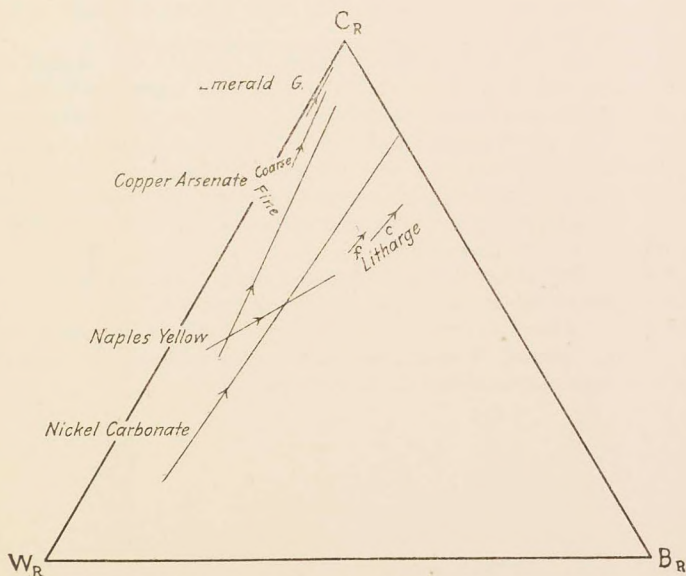


FIG. 6.—Wetting causes the color of these pigments to become more nearly pure and full. (See Section XV.)

FIG. 7.

Fig. 7 is designed to show changes in hue accompanying the addition of white or black pigments to colored paints (Sections XIII and XIV); but changes in purity and brightness are also indicated roughly. At the top the odd numbers 1 to 71 represent the Ridgway hues. Thus, intermediate hues between red (1) and orange (11) are 3, 5, 7, 9, and between violet (59) and red are 61, 63, 65 (purple), 67, 69, 71. In the upper part of the figure the colors are full, or nearly so, along the central horizontal line and grade upward (*b*, *d*, *f*) into clear tints, and into pure shades downward (*i*, *k*, *m*); in the lower part the colors are dull. Toward the top they pass into dull tints and toward the bottom into dull shades. (See Section V, last part.) *b* represents 9.5 per cent white; *d*, 22.5; *f*, 45; and *i* represents 45 per cent black; *k*, 70.5; *m*, 87.5. (See Fig. 2.) Circles, and sharp breaks in curves, represent the various colors before they have been modified by adding black or white. The curves marked "a" were produced by using a very fine-grain white, those marked "b", or not marked at all, by using a white containing few very fine grains.

The indices (') to (''') indicate that 32, 58, 77, and 90 per cent of Ridgway's neutral gray is present in the color besides the black or white represented by the letters.

Harrison red is a slightly dark orange-red (about 5 *i*). Added white scarcely affects the hue unless the white contains much very fine-grain material, in which case the hue changes to red (1 *f*'), and the tints produced are slightly dull. Black added causes the hue to become slightly more orange.

Yellow lake alone is a very dark orange-red (near 9 *m*). Added white causes the hue to migrate through orange to yellow. The color increases to a slightly dull orange-yellow, which then gives place to tints which become more yellowish as they grow lighter.

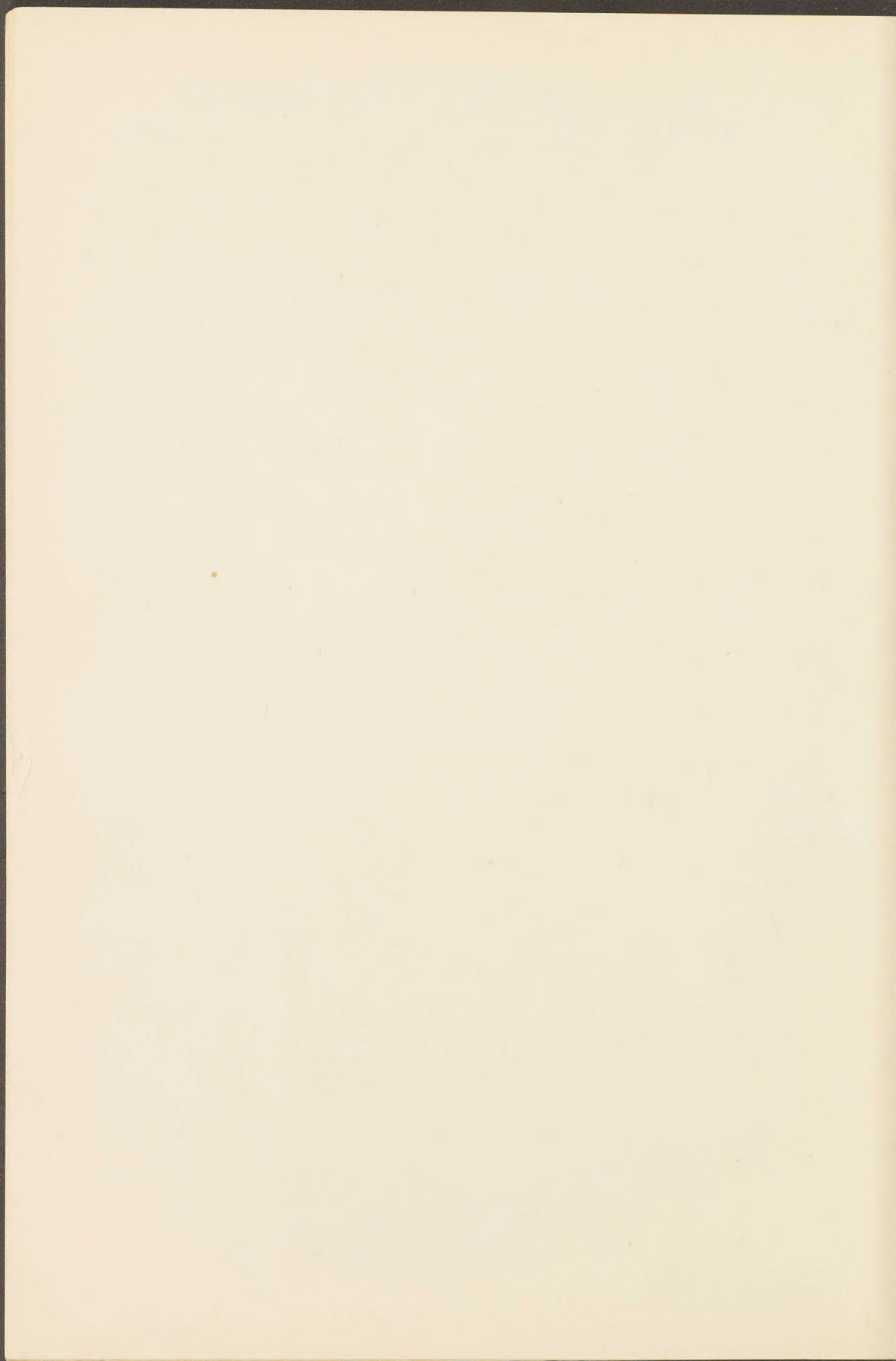
Lemon yellow (chrome) is a nearly pure, slightly orange yellow. White changes its hue to yellow, and black, to greenish yellow (27 *m*).

Note the difference between an even-grain cadmium orange and a darker, poorly ground, uneven-grain one. Also between a coarse-grain darker potassium chromate and one that is fine grained.



FIG. 7.





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